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Calcium anilate hexahydrate

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Anilic acid or 2,5-dianilinoterephthalic acid, $C_{20}H_{16}N_2O_4$, is an intermediate in the industrial synthesis of quinacridone pigments. The title calcium aniloate compound, namely di-μ-aqua-$\kappa^4O^1:O^{1'}$-bis(μ-2,5-dianilinoterephthalo-$\kappa^2O:O'$)bis[triaquacalcium(II)] tetrahydrate, $[Ca_2(C_{20}H_{14}N_2O_4)_2(H_2O)_8]\cdot 4H_2O$, is a dimeric complex of two aniloate anions, two Ca^{2+} cations and eight water molecules, with a further four uncoordinated water molecules. The complex is situated on a crystallographic twofold axis, with two water O atoms lying on the rotation axis.

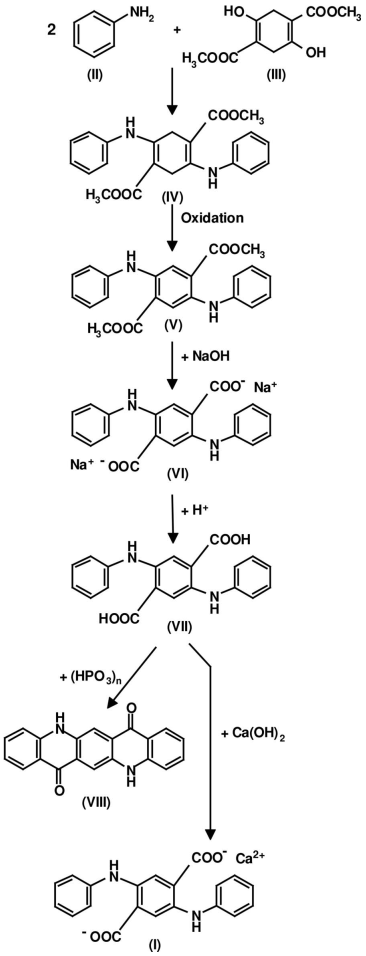
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.008 Å
H-atom completeness 74%
Disorder in solvent or counterion
R factor = 0.098
wR factor = 0.275
Data-to-parameter ratio = 12.4

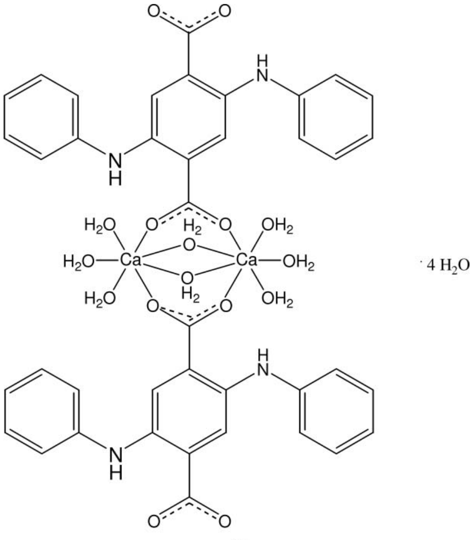
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

2,5-Bis(phenylamino)terephthalic acid, known as ‘anilic acid’ [first scheme 1, (VII)] in industry, is produced in amounts of over 1000 tons per year as an intermediate in the synthesis of quinacridone pigments.



Quinacridone (Pigment Violet 19, VIII) is the most important pigment for red–violet shades (Herbst & Hunger, 2004); it is used for automotive finishes, powder coatings, paints, plastics and high-grade printing inks. Recently, we determined the structure of anilic acid as a DMF solvate (Schmidt *et al.*, 2007), as well as the crystal structure of disodium aniloate decahydrate (VI) (Schmidt *et al.*, 2006) and the structures of three quinacridone polymorphs (Paulus *et al.*, 2007). Here we report the crystal structure of the corresponding calcium compound, (I).



(I)

The crystal structure of (I) contains dimeric units built up from two aniloate anions, two Ca^{2+} cations and eight water molecules, generated by a crystallographic twofold rotation axis (Fig. 1); four further water molecules are not coordinated. The calcium ions are coordinated by seven O atoms (Table 1), from two carboxylate groups, two bridging water molecules and three terminal water molecules. Surprisingly, one of the carboxylate groups coordinates to two Ca^{2+} ions, whereas the other carboxylate group is connected only by hydrogen bonds *via* water molecules to calcium ions of neighbouring dimers (Figs. 2 and 3). In addition there are four uncoordinated water molecules per dimer (Fig. 4). The unit cell contains eight formula units. The aniloate atoms are situated on general crystallographic positions. The aniloate anions are not planar; the terminal phenyl rings form dihedral angles of 33.47 (18) and 36.03 (19)° with the central benzene ring. The phenyl rings are twisted to the same side of the benzene ring, resulting in an approximate C_2 symmetry of the anion; this is in contrast to the structures of sodium aniloate (Schmidt *et al.*, 2006) and anilic acid DMF solvate (Schmidt *et al.*, 2007), where the aniloate units have approximate or exact inversion symmetry.

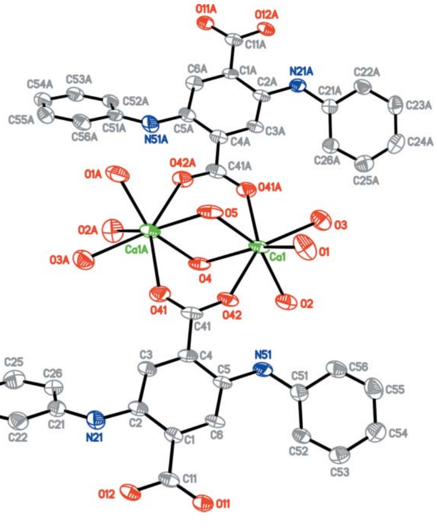


Figure 1
The structure of the dimeric complex (50% displacement ellipsoids; H atoms omitted for clarity). Atoms with the suffix A are generated by the symmetry operator $(1 - x, y, \frac{3}{2} - z)$.

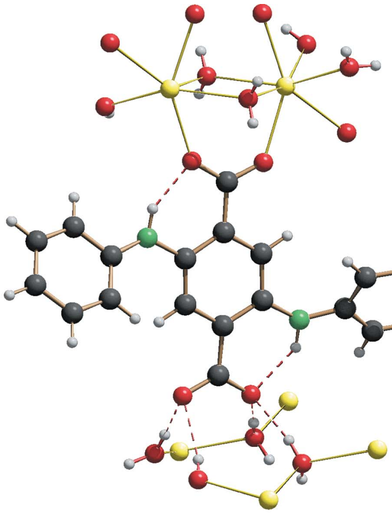


Figure 2
Detail of (I) showing the environment of the aniloate anion; one carboxylic group (top) is coordinated to two Ca^{2+} ions, whereas the other carboxylate group is connected only *via* O—H···O hydrogen-bonded (dashed lines) water molecules to the Ca^{2+} ions.

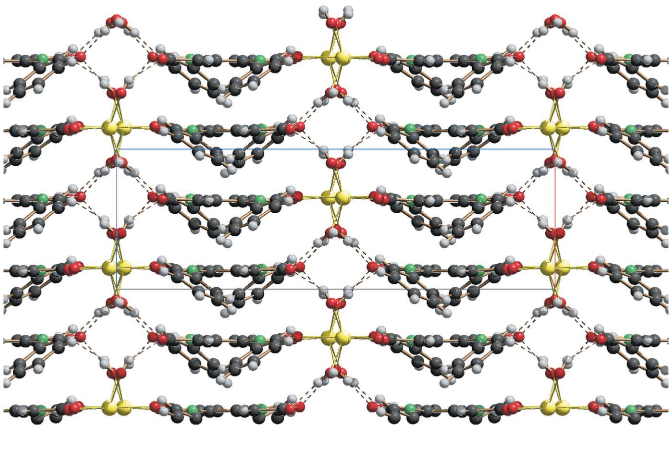


Figure 3
Packing diagram for (I). View direction [001]. H atoms have been omitted.

A network of O—H···O and N—H···O hydrogen bonds (Table 2) completes the structure of (I).

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Experimental

5 g of industrially produced 2,5-bis(phenylamino)terephthalic acid [anilic acid, (VII)] from Clariant, purified in the laboratory, was added to 0.5 l of saturated aqueous $Ca(OH)_2$ solution at room temperature. The mixture was stirred for 2 h at room temperature, and allowed to stand for 24 h; it was then filtered over a 20 µm filter to remove all particles. The solution was kept in a open 200 ml Erlenmeyer flask at room temperature for several weeks, allowing the calcium aniloate to crystallize slowly. Orange–red crystals of (I) as radial bundles with sizes up to 1 cm were formed. The crystals were separated by filtration, and carefully dried with tissue paper.

Crystal data

$[Ca_2(C_{20}H_{22}N_2O_4)_2(H_2O)_8]\cdot 4H_2O$
$M_r = 989.02$
Orthorhombic, *Pbcn*
$a = 22.4368\ (11)$ Å
$b = 7.1515\ (4)$ Å
$c = 28.9753\ (19)$ Å
$V = 4649.3\ (5)$ Å^3

$Z = 4$
$D_x = 1.413$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 0.33$ mm^{-1}
$T = 173\ (2)$ K
Plate, orange–red
0.23 × 0.17 × 0.09 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
$T_{min} = 0.929$, $T_{max} = 0.981$

48081 measured reflections
4117 independent reflections
3094 reflections with $I > 2\sigma(I)$
$R_{int} = 0.086$
$\theta_{max} = 25.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.098$
$wR(F^2) = 0.275$
$S = 1.14$
4117 reflections
332 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1038P)^2 + 27.6871P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.56$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ca1—O41^{i}	2.351 (4)	Ca1—O4	2.463 (4)
Ca1—O42	2.361 (4)	Ca1—O3	2.472 (5)
Ca1—O1	2.368 (5)	Ca1—O5	2.487 (4)
Ca1—O2	2.375 (5)		

Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*A*⋯O11^{ii}	0.839 (11)	2.02 (5)	2.773 (6)	149 (8)
O2—H2*A*⋯O11^{iii}	0.842 (10)	1.990 (18)	2.824 (6)	171 (7)
O2—H2*B*⋯O2*W*	0.840 (10)	2.23 (3)	3.045 (12)	163 (7)
O4—H4*A*⋯O12^{iv}	0.840 (10)	1.880 (13)	2.718 (6)	175 (7)
O5—H5*A*⋯O12^{v}	0.840 (10)	1.926 (17)	2.758 (6)	170 (7)
N21—H21⋯O12	0.881 (10)	1.93 (5)	2.633 (6)	135 (6)
N51—H51⋯O42	0.881 (10)	1.87 (4)	2.635 (6)	144 (6)

Symmetry codes: (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (v) $x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

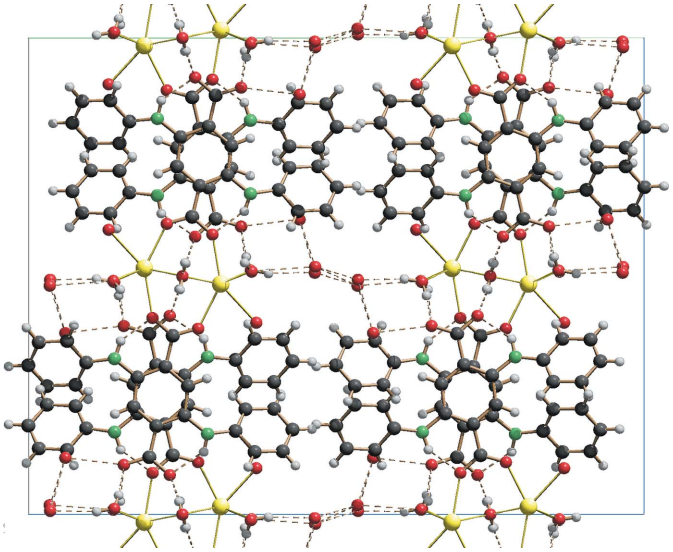

Figure 4
Packing diagram for (I). View direction [010].

The C-bound H atoms were positioned geometrically (C—H = 0.95Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N- and O-bound H atoms that could be located in a difference map were refined with a distance restraint of 0.88 (1)Å for N—H or 0.84 (1)Å for O—H. For the water H atoms, a distance restraint of 1.4 (3)Å for H⋯H was applied. Some water H atoms could not be located in difference maps, nor positioned geometrically, and were omitted from the refinement. One water O atom is disordered over two sites with site occupation factors of 0.66 (1) and 0.34 (1). The highest difference peak is 1.53Å from O2*W* .

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991) and *SCHAKAL* (Keller, 1999); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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